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PYROPHORICITY OF TRITIUM-STORAGE BED MATERIALS

G. R. LONGHURST

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Idaho National Engineering Laboratory
EG&G Idaho, Inc.
P.O. Box 1625
Idaho Falls, Idaho, 83425

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SUMMARY

Experiments were conducted on samples of depleted uranium and on intermetallic compounds of zirconium-cobalt and lanthanum-nickel-aluminide to evaluate the pyrophoricity of the activated materials and their hydrides and deuterides on exposure to air. It was found that none of the materials spontaneously ignited when exposed to room temperature air, but the uranium and the zirconium-cobalt both ignited in air at moderately elevated temperatures. Activated (dehydrided) materials showed stronger reactions than did the hydrides, but they ignited at essentially the same temperatures. Deuterides showed effectively the same characteristics as the hydrides except the ignition temperature of zirconium-cobalt deuteride was reduced by 20-50 K from that of the hydride. The possibility of a fire in tritium storage beds is real, especially if uranium or zirconium-cobalt are used as storage materials, but fires may not occur until the bed is heated.

INTRODUCTION

In a tritium-burning fusion reactor facility, the largest inventory of tritium will be in the fuel-storage system. In the TIBER II/ETR final design for example, of the 1700-3600 g of tritium (as T_2, DT, HTO or metal tritide) expected to be in the system, 1000-2000 g of tritium is expected to be in metal getters in the fuel storage system.[1] One of the principal safety concerns of such systems relates to hazards associated with the accidental exposure of the storage bed to air. Uranium, the metal most often used in the past for tritium storage, is known to be pyrophoric in air, particularly after it has been activated by forming the hydride, deuteride, or tritide.[2] When exposed to air at ambient or moderately elevated temperatures, a rapid chemical reaction takes place with the release of approximately 320 kJ/gmole. This results in the evolution of such tritium as may be on the bed, converting it to the more hazardous oxide form. Damage to the storage bed may also result, including possible rupture and attendant dispersal of tritiated materials and uranium.

Other materials are being considered for use in tritium-storage systems including zirconium-cobalt and lanthanum-nickel alloys. The latter appear to be significantly less pyrophoric than uranium while still maintaining desirable equilibrium pressure-temperature characteristics. By appropriately modifying the composition of the lanthanum-nickel alloy with aluminum or manganese, the tritium solution isotherms may be tailored to exhibit almost arbitrary pressure-temperature characteristics with respect to hydrogen solution.[3,4]

Accidents, such as the rupture of the container by a missile or by dropping or unintentional opening of the container to air, must be considered in safety analyses. Such analyses require fairly detailed information regarding the chemical response exhibited by these reactive metals when exposed to air or other atmospheres.

EXPERIMENTS

To help in the design and planning for tritium storage and transportation using reactive metal beds, a series of experiments was undertaken in which the objective was to observe the response of materials of interest when they were exposed to air. These experiments were conducted on small samples of uranium, zirconium-cobalt, and lanthanum-nickel-aluminide.

Apparatus

The experimental apparatus is shown schematically in Figure 1. The principal element is a Du Pont 951 Thermogravimetric analyzer (TGA).[a] It is a microbalance housed within a quartz tube assembly which may be inserted into a temperature- and temperature-rate programmable tube furnace. A gas circulation loop containing a pair of MKS Baratron capacitance manometers (133 kPa and 133 Pa full range) is attached. These

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[a] Mention of specific products and/or manufacturers in this document implies neither endorsement or preference nor disapproval by the U.S. Government, any of its agencies, or EG&G Idaho, Inc., of the use of a specific product for any purpose.

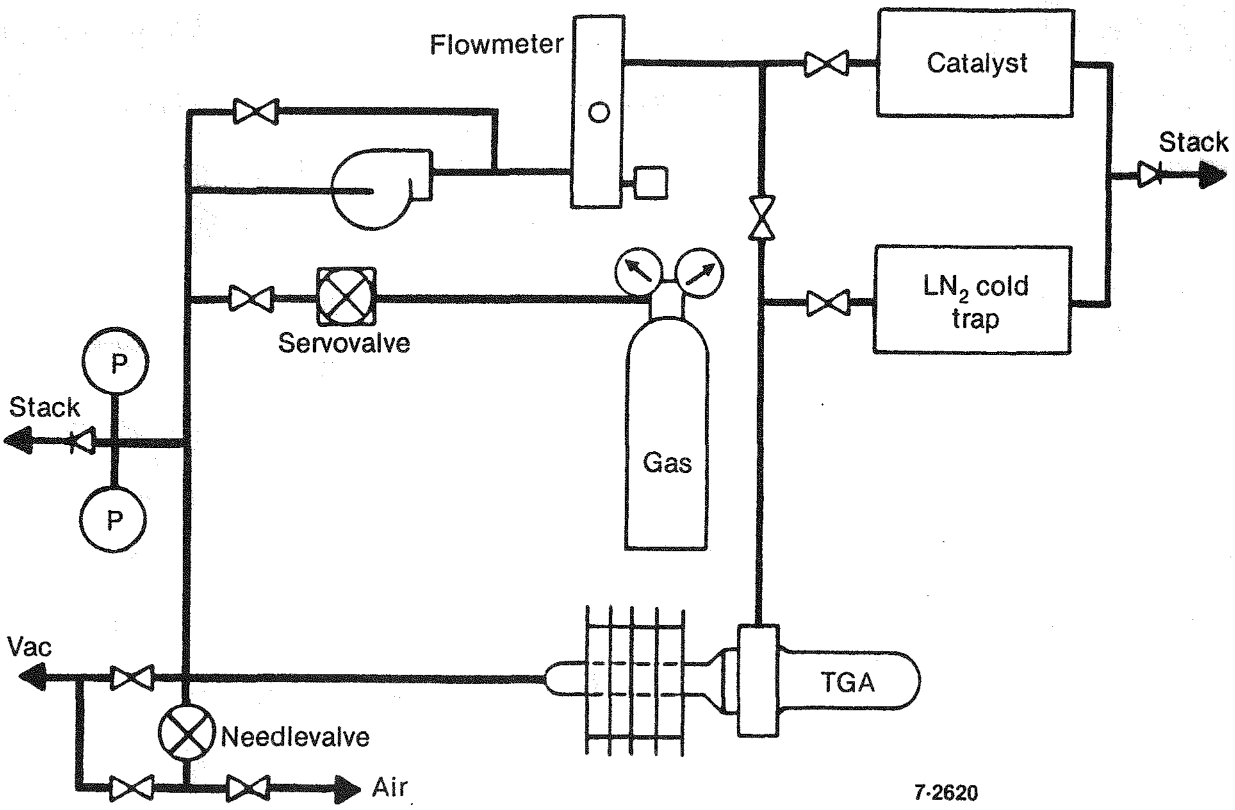

Figure 1. Schematic of the experimental apparatus used in pyrophoricity experiments.

manometers, with their associated electronics, control a Granville-Phillips Series 216 servovalve which allows the loop to be maintained at a predetermined constant pressure. A Metal Bellows MB-21 pump is used to circulate hydrogen or deuterium gases through a flowmeter (150 mL/min full scale). A catalyst bed (Engelhard Deoxo hydrogen purifier) followed by a LN_2-cooled cold trap is used to remove residual oxygen and other condensable or burnable gases from the hydrogen stream.

On these experiments, the TGA thermocouple was inside the sample pan, approximately 2 mm or less from the sample. Direct thermocouple contact with the sample was not possible because of interference with the microbalance function. This was evident in some uranium tests where swelling of the sample caused it to contact the thermocouple giving a false weight reading.

Procedure

The typical procedure for the tests was to place approximately 30-100 mg of the reactive metal into the sample pan of the TGA. In the uranium tests this was a single piece cut from 0.5-mm-thick sheet, cleaned in 50% nitric acid and washed in ethanol. The other materials were supplied as powders, the zirconium-cobalt by the Japan Atomic Energy Research Institute and the lanthanum-nickel-aluminide by the Savannah River Laboratory. These were used in the as-received condition. After weighing the sample using the TGA, the Du Pont 990 Thermal Analyzer used to control the TGA and monitor the output was set to record weight changes as a fraction of the sample weight. The system was evacuated and all the gas loop except the TGA was heated to approximately 380 K using heater tapes for 1-3 h. The duration depended on the amount of adsorbate on the walls as evidenced by the pressure history. If the system had not received significant air exposure, the pressure dropped rapidly, and heating for long periods was not required.

After cooling to room temperature and filling the cold trap with LN_2, the system was filled to 86.5 kPa (ambient pressure was 85.2 kPa) with hydrogen (or deuterium) which was then circulated through the purifier and cold trap for 15 min. This was long enough to accomplish 5 volume changes in the system. At that point the pump was stopped and the purifier and cold trap were valved out. On some tests the purifier and cold trap were left in the circuit to scavenge impurities, but that proved to be an undesirable source of oxygen. The specified number of heating cycles was then induced. The temperature range varied with material but was sufficient to induce essentially complete solution and evolution of hydrogen on the material, bracketing the equilibrium temperature for the hydrogen pressure.

If the sample was to be exposed to air in the hydrided condition, it was cooled to room temperature at constant hydrogen pressure, then the system was evacuated to about 100 Pa before air was added. Evacuation to lower pressures tended to cause hydrogen loss in the sample. If testing was to be done on dehydrided material, the system was evacuated at the high temperature in the cycle, then cooled to room temperature before air was admitted. In most tests a small degree of rehydriding occurred when the sample was cooled because of the slight hydrogen pressure due to loop outgassing. This was confirmed by additional temperature cycling under vacuum. Occasionally, there were small air leaks through one of the pressure-relief valves which tended to degrade the quality of the sample prepared.

Air was admitted slowly (1 kPa/s) so that the drafts in the TGA would not disturb the weight reading. The temperature was then ramped, usually at 10 K/min, to 873 K or until it was evident from the stability of the weight measurement that oxidation had progressed to completion. Visual observation was made of the sample through the end of the quartz furnace tube during periods of high chemical activity to look for incandescence and swelling.

Initial plans had been to expose the samples to nitrogen as well as to air. This was not done for two reasons. First, the accident scenario considered was specifically an air leak. That would have more serious consequences than leakage of a nitrogen atmosphere in a secondary containment. Second, in previously conducted experiments[5] it was found that exposure of uranium to nitrogen differed from oxygen exposure mainly in the energy released and the formation of the nitride rather than the oxide. Hence, it was judged less worthwhile to pursue the nitrogen testing than to look at other air conditions within the limited scope of the project.

RESULTS

General

No weight gain was seen on air addition to the system on any of the tests, nor was there a disturbance in the temperature. It was concluded that there was no immediate reaction to room-temperature air.

When there was a reaction, after samples had been heated above ambient temperature, it was evidenced by a sudden indicated temperature rise and gain in weight. Figures 2 through 4 show characteristic traces for each of the materials tested. Temperature rise times varied from a few tenths to approximately one second. Indicated mass rise times were slightly longer, but this is believed due to the response characteristics of the TGA and its controller. Visual observation of reactions ranged from a sudden, bright flash similar to the toggling of an incandescent lamp, to a more gradual heating to luminosity and then cooling. The temperatures indicated by the TGA thermocouple often reached 1000-1200 K, but were lower than actual temperatures because of the thermal mass of the sample pan, the associated air, and the thermocouple. In most uranium tests the platinum sample pan was melted (2045 K). The temperature attained during a reaction depended on the mass of the sample, with the more massive samples reaching higher temperatures.

Weight increases observed were of two types. During the reactions, there were sudden and emphatic shifts corresponding to the severe temperature spikes. Depending on the material, the weight change was an

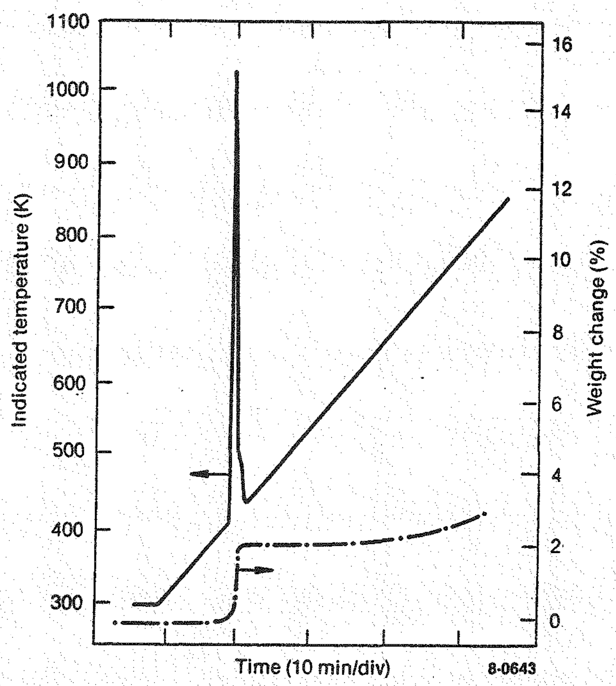

Figure 2. Characteristic response of uranium hydride to air exposure and heating.

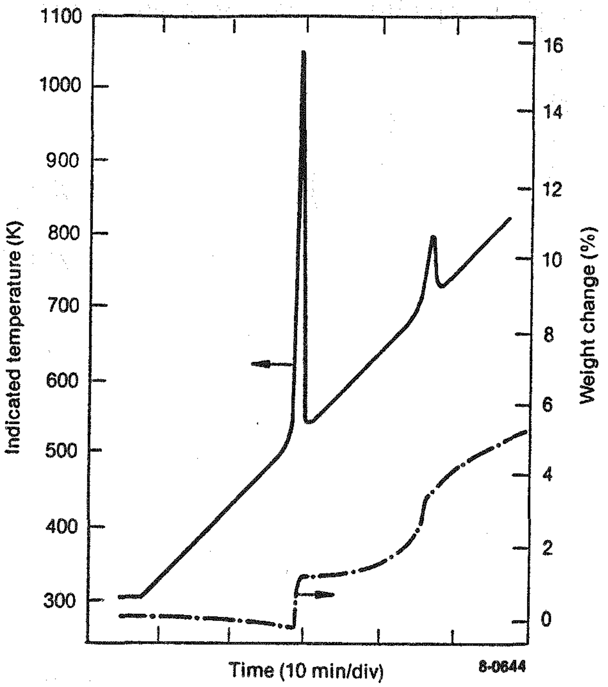

Figure 3. Characteristic response of zirconium cobalt and its hydride to air exposure and heating.

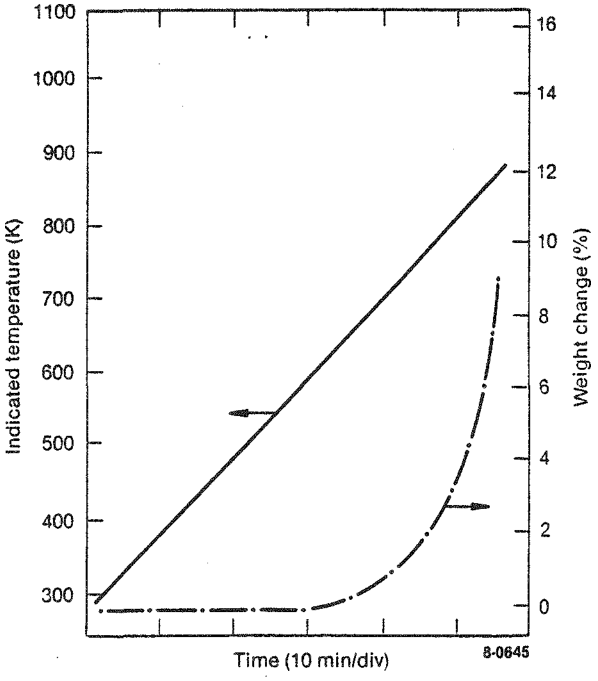

Figure 4. Characteristic response of lanthanum-nickel-aluminide to air exposure and heating.

abrupt step function to a plateau or a marked steepening with more gradual weight gains before and after. Figures 2 through 4 also show typical weight gain profiles for the three materials tested.

In some tests, there was also a slow background rise in sample weight during the hydriding cycles which was material and temperature dependent. This slow rise was most evident during hydriding on uranium tests because the temperatures required for dissolution of the hydride were higher (reactions proceed faster at higher temperatures), and uranium has a greater affinity for reactive gases than the other metals tested. This slow gain was not evident in the lanthanum-nickel-aluminide tests. In the uranium tests requiring vacuum conditions at elevated temperature, the rate of rise corresponded with formation of oxide at 20% of the measured apparent leak rate. The source of the contaminant was not determined with certainty. Helium leak checking was performed, but no detectable leaks were observed down to the threshold of the instrument (10^{-9} scc/sec). It was postulated that leaks were mainly due to backflow through pressure relief valves included in the design of the system for protection of the Baratrons. However, the system was at a positive pressure with respect to local atmospheric pressure during the hydriding cycle. It isn't obvious that that much molecular backstreaming would exist under those conditions. Another possibility is that the contaminants were being generated by the action of the hydrogen on the components of the TGA or by their outgassing. Determination of the exact nature of the contaminants by the various analytical tools available at the INEL was not pursued. This was partly because of the limited scope of the current project and also because of the administrative difficulty in transporting the radioactive uranium from the location of the experimental apparatus (TRA) into the laboratory housing the analytical tools (IRC) located in Idaho Falls.

Principal results for the individual materials are summarized in Table 1. There are listed for each of the tests conducted the material and sample weight, the hydriding conditions (hydrogen isotope used, number of hydriding cycles, and hydrogen-to-metal ratio when exposed to air), the heating rate applied during the air exposure, the ignition temperature for the strong reactions observed, and the composition produced in those

TABLE 1. SUMMARY OF EXPERIMENTAL CONDITIONS AND RESULTS

			Hydriding						
No.	Mat'l	Wt.(mg)	Gas	Cyc.	H/M	Heat Rate (K/min)	Reaction Temp.(K)	Composition Produced	Remarks
1	U	32.8	H_2	5	3.0	20	423 573	UO_2 U_3O_8	$UO_{0.88}H_{0.36}$ before reaction. 2nd reaction unusual for U.
2	U	55.1	H_2	5	3.0	10	428	UO_2	$UO_{0.37}H_{1.89}$ before reaction, slow conversion to U_3O_8 as T-->673 K.
3	U	42.9	H_2	6	~0	10	468	U_3O_8	$UO_{1.58}$ before reaction.
4	U	31.0	H_2	5	~0	5	448	U_3O_8	$UO_{0.42}$ before reaction.
5	U	46.0	D_2	5	3.0	10	443	UO_2	$UO_{0.5}D_{2.23}$ before reaction.
6	U	36.5	D_2	4	~0	10	443	UO_2	0.6% irreversible weight gain before reaction.
7	ZrCo	62.4	H_2	4	2.8	20	553 613	$ZrCoO_{0.65}$ $ZrCoO_{1.0}$	0.056 oxygen mole fraction before 1st reaction.
8	ZrCo	45.9	H_2	4	2.8	10	558 758	$ZrCoO_{0.79}$ $ZrCoO_{1.83}$	2nd reaction at higher temperature than No. 7.
9	ZrCo	91.0	H_2	4	0.75	10	553 678	$ZrCoO_{1.04}$ $ZrCoO_{1.58}$	0.033 oxygen mole fraction before 1st reaction, still climbing after 2nd.
10	ZrCo	58.1	None	0	2.3	10	488 588	$ZrCoO_{0.71}$ $ZrCoO_{1.29}$	Hydrogen just beginning to evolve as 1st reaction occurred.
11	ZrCo	60.4	H_2	1	2.8	10	558	$ZrCoO_{1.35}$	Multistage reaction over range 558-603 K.
12	ZrCo	56.1	D_2	4	2.5	10	538	$ZrCoO_{1.26}$	Gas (9%) evolved prior to reaction, some isotope exchange evident on 1st heating.
13	ZrCo	69.1	D_2	1	2.6	10	503 703	$ZrCoO_{1.05}$ $ZrCoO_{1.80}$	Gas (6%) evolved prior to reaction, isotopic exchange on 1st heating.
14	LaNiAl	48.7	None	0	0	10	-	-	No sharp reaction, goes to $LaNi_{4.25}Al_{0.75}O_{18.8}$.
15	LaNiAl	47.2	H_2	5[a]	0.4	10	-	-	60% of gas evolved before oxidation began (560 K)
16	LaNiAl	99.9	D_2	4	0.35	10	-	-	Same as No. 15.
17	LaNiAl	71.3	D_2	5	0.8	10	-	-	Most D_2 evolved before oxidation occurred.

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[a] Also 4 pressure driven cycles at room temperature.

strong reactions. Compositions shown in Table 1 were calculated assuming oxidation for all irreversible weight gains and hydriding (deuteriding) for all those reversible under temperature variations. Specific observations and comments are as follows:

Uranium

A published[6] comparison of the thermodynamics of UH_3 and UD_3 indicates that at 87.9 kPa in H_2 the equilibrium temperature of UH_3 should be 696 K while that in UD_3 should be 681 K at the same pressure. The enthalpies of formation of both compounds are shown as identical. During the hydriding phase of these experiments, formation of UH_3 commenced at 662 K during the cooldown part of the cycle while dehydriding started at 713 K during heating. The average of these is 687.5 K which is in fair agreement with the published result. The deuteriding cycle obtained is shown in Figure 5. Hydriding showed a similar curve with higher temperatures as indicated. The hysteresis is due to the temperature rate effects (20 K/min). One would expect a shift to the lower side of the equilibrium temperature under these conditions because

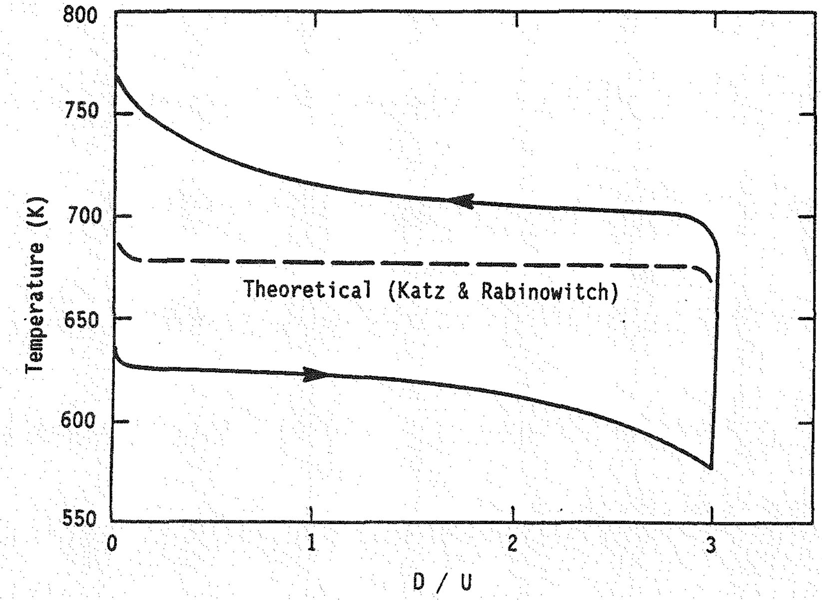


Figure 5. Composition cycle observed during preparation of UD_3. The cycle for UH_3 is similar but at a 20 K higher temperature.

transport is slower at lower temperatures, and a greater departure from the equilibrium temperature would be expected to be needed to drive the phase change. For the UD_3 the formation and dissolution temperatures were 628 K and 706 K, respectively. The average of these, 667 K, is 20 K less than that for UH_3, about the same difference as in the published data referred to. In these experiments, the temperature perturbation experienced during phase changes was about 20% more pronounced with deuterium than with protium. This may be simply the result of slight differences in thermocouple placement. There was no distinguishable difference in the rates of hydriding and dehydriding between UH_3 and UD_3 once each process had begun.

The slow background drift in weight during the hydriding process is illustrated in Figure 6. It may also be concluded from the shapes of the hydriding weight transients that the activation process, or the breaking down of the material from the starting integral chip to the fine powder characteristic of activated uranium and UH_3, was essentially complete after the second hydriding cycle. The lessening of the weight change observed in successive cycles is related to the slow irreversible weight

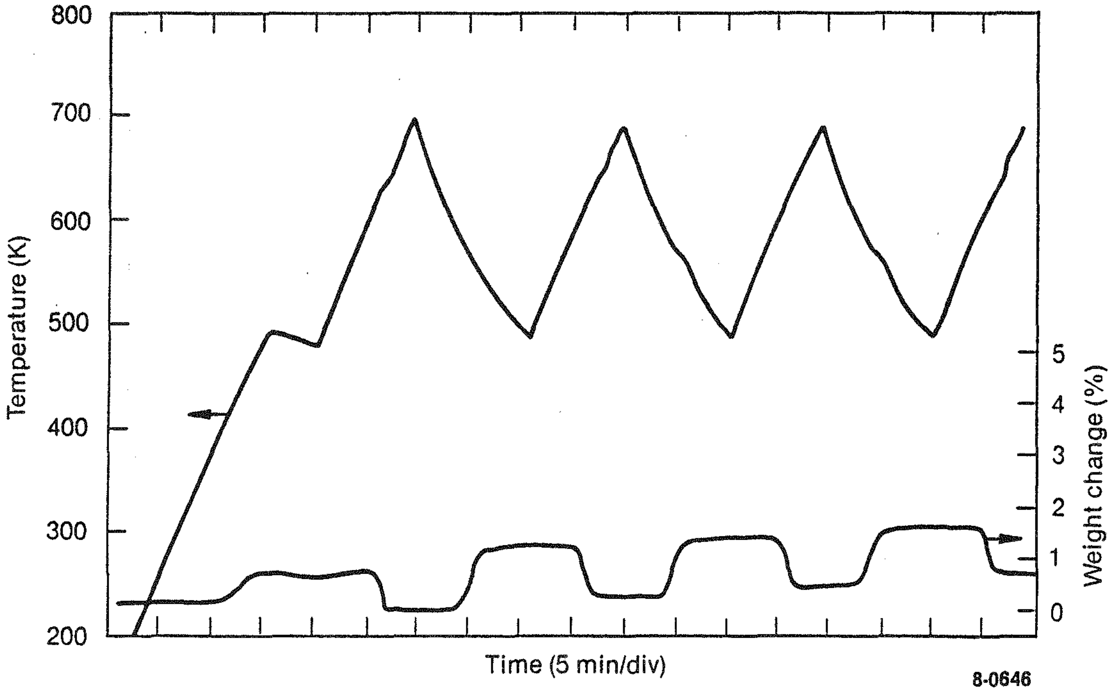


Figure 6. Hydriding transients observed in the preparation of UH_3.

gain. Less of the uranium is available for participation in hydriding. The diminution is consistent with the assumption that oxide formation is responsible for the irreversible weight growth.

Water formation was evident immediately following the strong reactions in tests of uranium with both hydrogen isotopes. It was observed as condensation on the cooler parts of the quartz furnace tube. Reactions of the hydrides of both hydrogen isotopes were very brisk, with the temperature excursion and luminosity lasting just a few tenths of a second. Temperatures were high enough to melt the platinum sample pan. Such a pan is shown in Figure 7. With both hydrogen isotopes oxidation of the hydride produced UO_2 initially followed by the gradual conversion to U_3O_8 with increasing temperature (see Figure 2). When activated but dehydrided metal was heated in air, the reaction went to U_3O_8 directly.

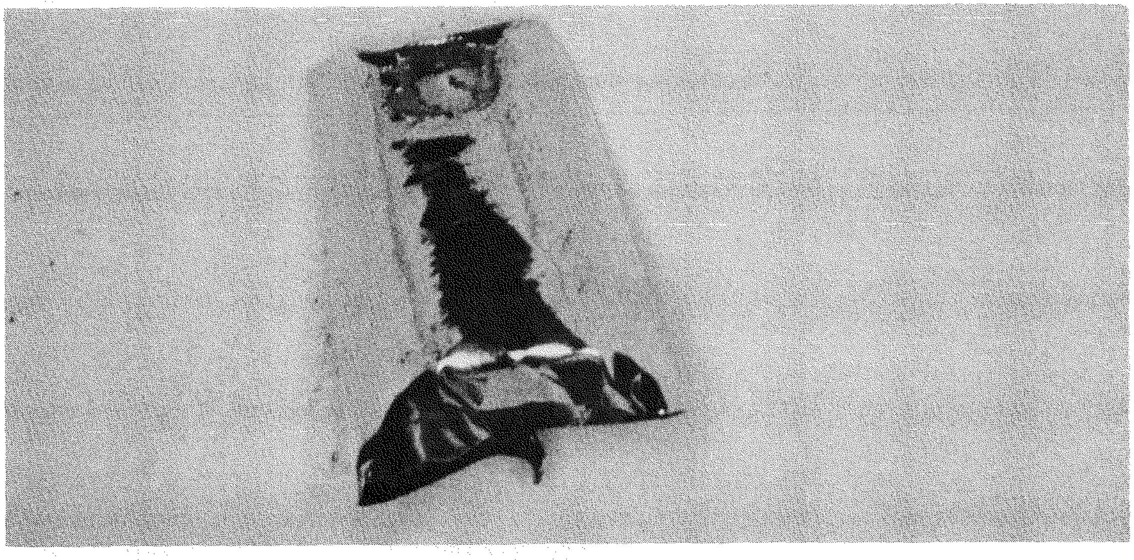
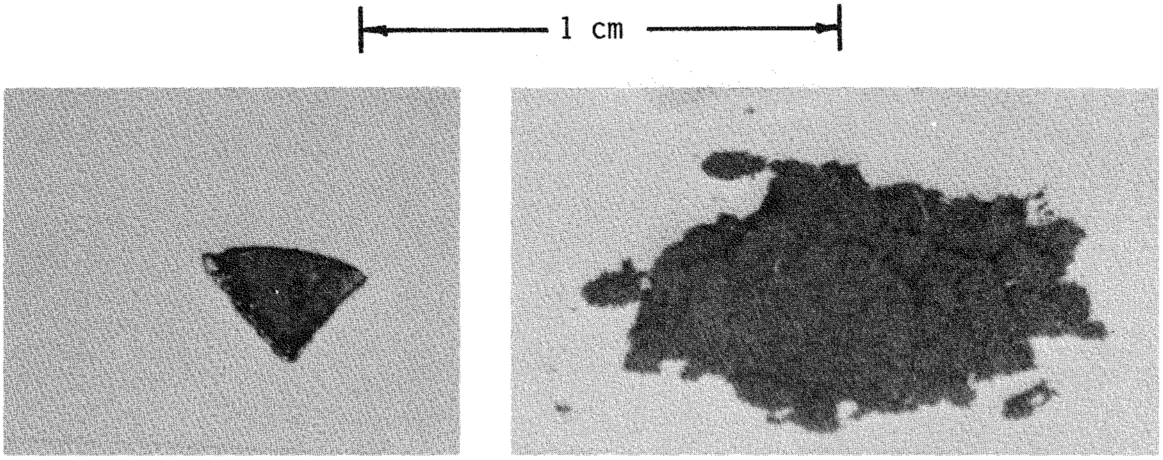


Figure 7. Hole burned in a platinum sample pan by burning UH_3.

It is generally conceded that activated uranium, and to a lesser extent the hydride, are pyrophoric at ordinary temperatures in air.[2] No spontaneous ignition in air at room temperature was seen in these experiments. This was consistent with previously reported, similar experiments.[5] As indicated in Table 1, for both fully hydrided and mostly dehydrided uranium, combustion did not take place in air until the temperature had been elevated to about 440 K. A probable explanation is that because of low but finite oxygen (and/or other contaminant) partial pressures in the system during the hydriding phase, partial irreversible reaction of the extremely reactive uranium took place before deliberate exposure to air. An irreversible weight gain during the hydriding process of 0.5-2% was observed on most uranium tests. Thus, up to 20% of the uranium could have been oxidized or otherwise reacted during the hydriding cycles, certainly a large enough fraction that the exposed surface of the uranium grains could be covered. This would have stifled the room-temperature reaction to the point that ignition would not have occurred.

One complication associated with use of uranium in storage beds is that there is a significant volume expansion on hydriding. Figure 8 shows this graphically. The uranium was visually observed to swell markedly on hydriding and collapse as the hydrogen came off. This was not evident on the tests of the other materials. Even greater uranium swelling was manifest during the oxidation stage of the experiments. Sometimes this resulted in the pushing of the powder over the edge of the sample pan or pushing on the thermocouple to give false weight-gain readings.



(a) (b)

figure 8. Demonstration of the volume change evident in the hydriding and oxidation of uranium: (a) solid metal, (b) powdered oxide. Starting uranium weight was approximately 36 mg.

Zirconium Cobalt

Oxidation during hydriding was far less a problem with zirconium-cobalt than with uranium. Irreversible weight growth was typically less than 0.5% suggesting an oxygen/metal ratio of less than 1% when air exposure was initiated. Hydriding temperatures followed closely published isotherms,[7] again with some hysteresis evident due to temperature rate effects. Typical hydriding and deuteriding curves for zirconium-cobalt are shown in Figure 9.

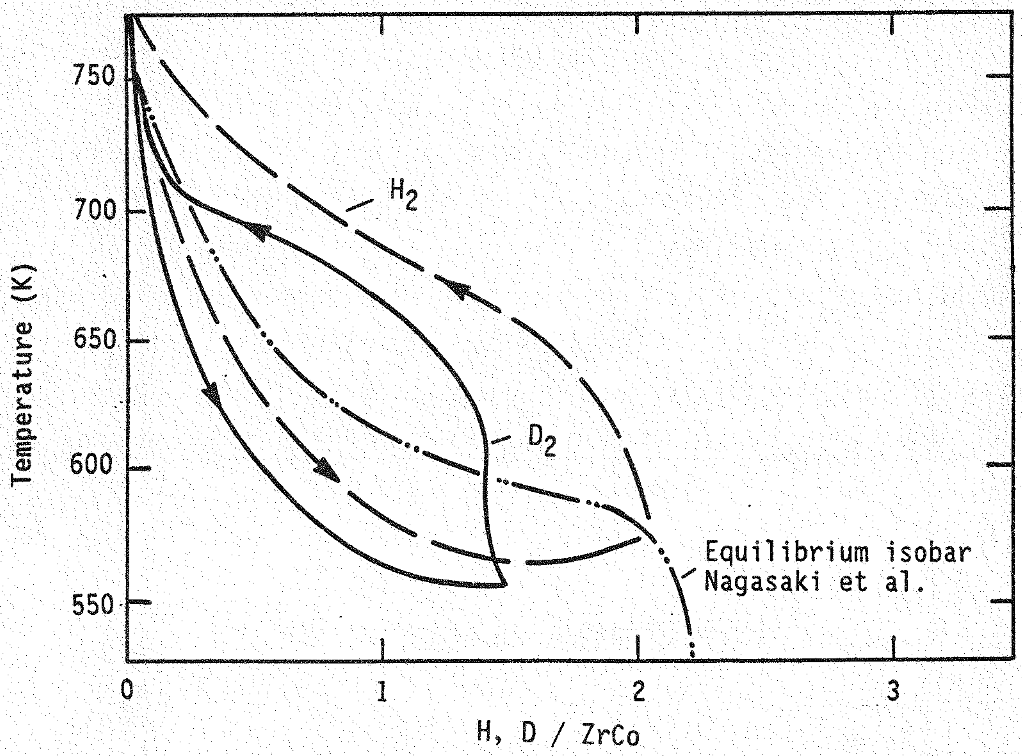
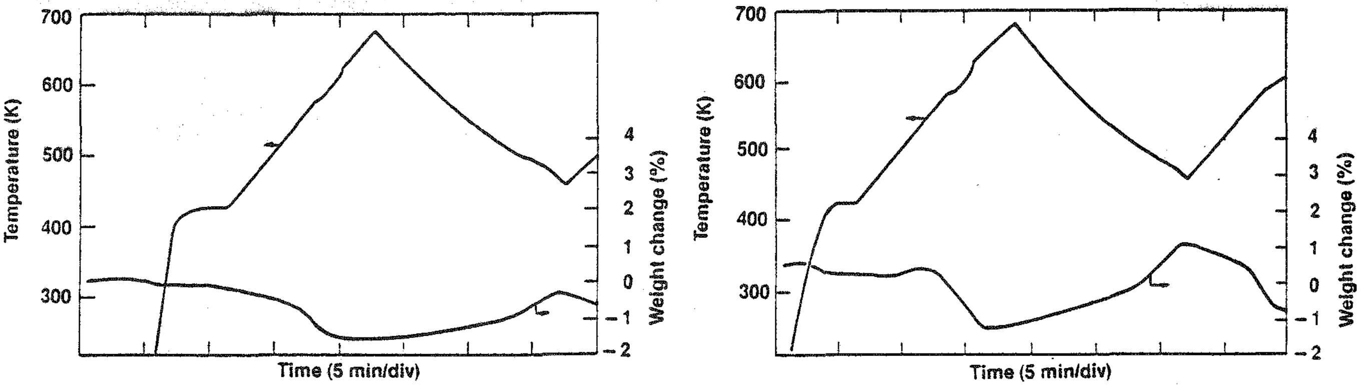


Figure 9. Representative hydriding and deuteriding cycles for zirconium-cobalt in 88 kPa gas.

It became evident that the zirconium cobalt furnished came as a hydride. This was clear because the first weight change on heating was a loss rather than a gain as was typical with uranium. Furthermore, when heated in deuterium, the first gain following the loss was effectively as much above the initial weight as the first loss was below it. This may be interpreted as isotopic exchange. Figure 10 shows the raw data. It is also interesting that some isotopic exchange is evident even before the first dissolution of the hydride.



Initial transient in H_2

Initial transient in D_2

Figure 10. Isotopic exchange was evident on deuteriding of the zirconium-cobalt received.

Typical thermochemical response of zirconium-cobalt is shown in Figure 3. It was characteristic of this material to exhibit two sharp reactions after hydriding, but the ignition temperatures and relative intensities were not consistent. In the case of the the as-received sample (No. 10 in Table 1) the two reactions were of equal intensity as determined by temperature excursions. After a single temperature cycle in deuterium (No. 12) the second temperature excursion was greater than the first (420 K versus 255 K indicated), but the first lasted for approximately five minutes while the second had cooled after only one minute. When more than one hydriding cycle had been undertaken, results were different yet. After four hydriding cycles in H_2 (No. 8 in Table 1 and Figure 3), two distinct reactions were present; but the second temperature excursion was only 80 K above ambient while the first one indicated a change of 730 K. After four cycles in deuterium (test No. 12), only the first reaction appeared.

These differences in response are probably related to the physical structure of the material grains. Temperature cycling in hydrogen tended to produce sintering or grain agglomeration. The distribution of weight gains and energy release over the temperature ramps in air was probably due to variations in structure caused by this sintering.

Evolution of gas was observed to begin at a temperature 50 K below that where the first reaction took place in all the zirconium-cobalt samples tested except the one in which most of the hydrogen had been driven off. When ignition occurred, there was a very sharp transition in mass. On the other hand, in the dehydrided sample test (No. 9 in Table 1), there was a gradual onset of weight gain before the oxidation reaction ignited, similar to the weight gain seen in the air exposures of uranium. It appears that the oxidation of the hydrogen evolved may first delay, then accelerate the burning of the zirconium-cobalt, though it may also be the solution of surface oxide films that keys ignition.

No particular swelling was observed in the sample during hydriding or oxidation stages of the tests. The grain size of the oxidized material appeared to be about the same as at the start, except for the sintering that sometimes left a large lump in the center where temperatures were the highest. There was visible bonding of the oxidized zirconium-cobalt to the platinum pan. Many of the grains contacting the pan stuck there and could only be removed by comparatively firm scraping.

Lanthanum-Nickel-Aluminide

A typical hydriding cycle seen for the lanthanum-nickel-aluminide is shown in Figure 11. Also shown there are published isobars for equilibrium states of two similar lanthanum-nickel-aluminum alloys. The solubility of hydrogen in these alloys is such that the initial hydriding took place at room temperature, before the heating cycles were begun. Because of the low temperatures for the phase transitions, there was really not adequate time allowed for hydrogen to devolve and move from the sample during the hydriding cycles imposed. On subsequent tests planned, this will be corrected.

A major observation regarding these experiments is that there was no strong reaction in air, even at high temperatures. The oxidation characteristics are similar to those of titanium. From that perspective

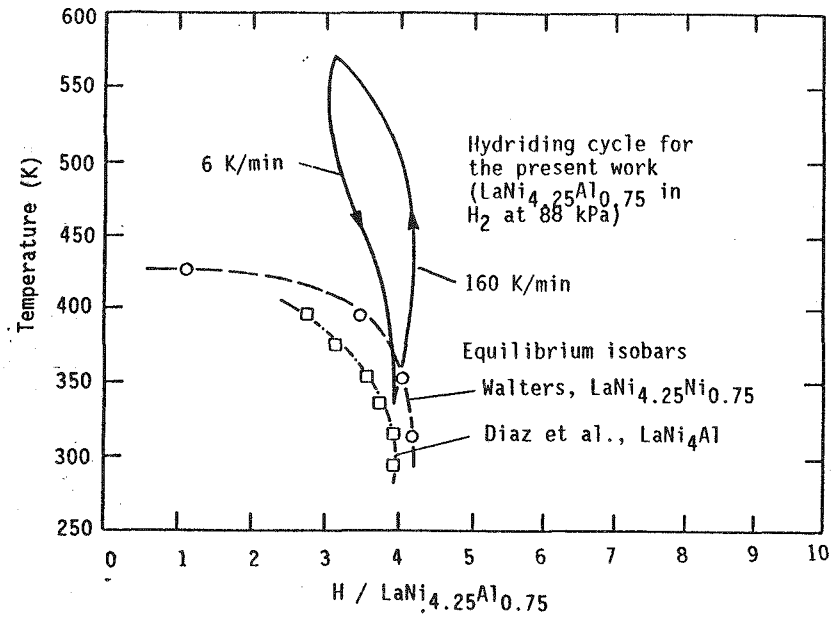


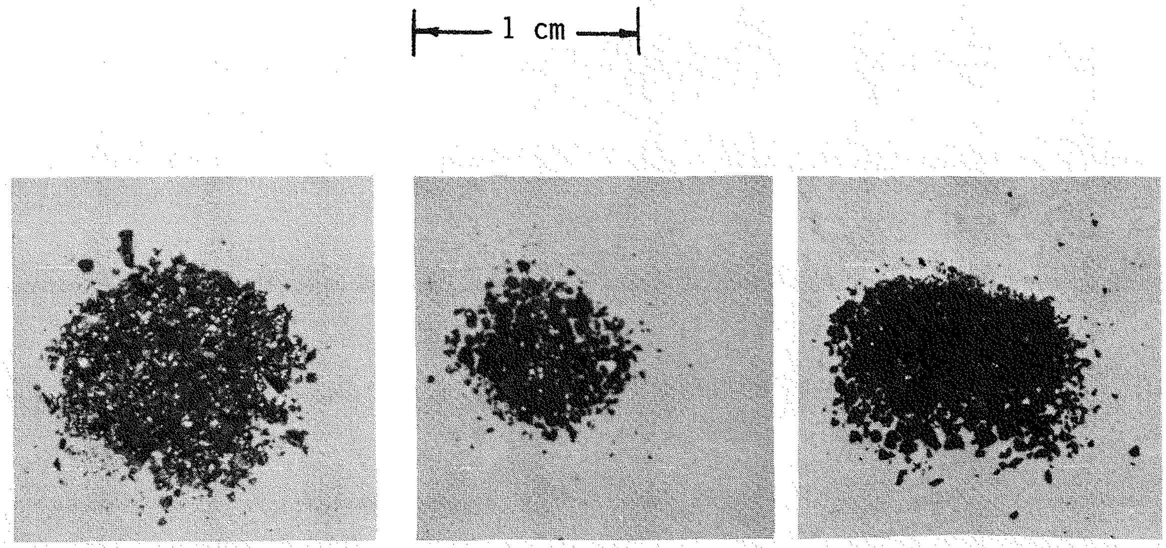
Figure 11. Hydriding cycle observed for lanthanum-nickel-aluminide.

it is an excellent choice of material for tritium storage beds. No significant isotopic effects were observed. Essentially complete gas evolution was noted prior to the onset of oxidation, but there were no particular consequences of that.

Considerable grain size modification was associated with the oxidizing process, though it did not appear during the hydriding, probably because of the incomplete extent of the hydriding as shown in Figure 12. Material that started as coarse granules, up to 1 mm in diameter mixed with finer powder, appeared as fine, uniformly-sized granules, approximately 100 um in diameter, after oxidation. Figure 12 compares the appearance of these phases.

DISCUSSION

These experiments modelled the accident in which a slow air leak occurs in a tritium storage bed. Particularly in the uranium tests, it was not possible to admit air suddenly because the draft would dislodge



(a) (b) (c)

Figure 12. Comparison of the phases of lanthanum-nickel-aluminide observed in these experiments: (a) as received, (b) after hydriding, and (c) after oxidation.

the fluffy hydride powder from the sample pan, and no weight measurement would then be possible. (Viscous drag forces from even slight drafts disturb the weight measurement on all tests.) Should an air-leak accident occur with a uranium bed or a zirconium-cobalt bed, and the bed be unwittingly heated with air in it to generate tritium, substantial damage to the bed may result. In most of the uranium tests there was melt-through of the platinum sample pan, and in the zirconium-cobalt tests there was sufficient melting of the platinum that granules of material were effectively bonded to the pan.

A bed containing 1 kg of uranium tritide, if ignited, could release approximately 6 MJ; more than enough energy to melt a 10-kg bed structure. A saving design feature may be restrictions on air getting to the uranium. For the situation just described, approximately 0.8 m^3 of air would be required for stoichiometric combustion. This is more air than would probably have access to the uranium. Depending on the location of the leak and the lengths of feed lines connected to the bed, that much air may not be available for combustion. However, if only 10 L of air were available, 70 kJ could be released which may still produce local structural damage.

No room-temperature pyrophoricity was seen in these tests for any of the materials. Others' experiences[8,9] suggest this may be a problem for uranium or zirconium-cobalt if there is no oxide film on the surface. In the event of a sudden, catastrophic failure of a tritium-storage bed using these materials, there would be turbulent mixing of the powdered reactive metal with the inrushing air. In that circumstance, any stabilizing effect of surface films may be dominated by the exposure of clean reactive metal surface, and ignition may not require external heating.

CONCLUSIONS

These experiments were a fair simulation of the accident scenario in which a slow air leak into a tritium storage bed is followed by inadvertent heating of the bed. In actual tritium storage systems there will probably be some oxygen and nitrogen contamination, though probably less than was present in these experiments. The small amount of reactive metal, compared with the volume of the test loop, resulted in exaggerated response to these contaminants over what would be evidenced in a working tritium-storage system. This may be the reason that no room-temperature pyrophoricity was observed, but uranium and zirconium-cobalt and their hydrides and deuterides all exhibited very strong chemical reactions in air when heated to moderate temperatures. No such reactions were observed with lanthanum-nickel-aluminide.

As tritium storage bed material, lanthanum-nickel compounds are recommended as superior to the other two materials in their safety aspects. Burning of zirconium-cobalt may be expected to release about one-third the energy per mole of the uranium reaction. Hence, zirconium-cobalt would be a better choice of material than uranium. Lanthanum nickel alloys would be better yet because no rapid energy release would be expected in an accident of the type assumed.

Hydrogen-isotope effects do not appear to strongly influence the pyrophoric response of the materials tested. With respect to their burning characteristics, the only significant hydrogen-isotope-dependent effect observed was a lower ignition temperature by 20-50 K for zirconium-cobalt deuteride than for the hydride. Differences in the solution characteristics of the two isotopes of hydrogen in uranium were seen, but these do not seem to effect ignition. No such differences were observed in the other two materials.

Should beds be used that contain either of the other two materials, care should be exercised to minimize the free volume which may be accidently filled with air to which the reactive metal may be exposed. This may be accomplished by placing valves close to the bed and keeping the free volume inside the bed canister small.

Most tritium storage beds may be expected to evolve tritium to some low pressure consistent with their temperatures in the course of time, even if they were initially placed under vacuum. Should hard vacuum be maintained, the tritium would eventually be pumped from the system. The possibility that air may exist in the storage bed, its pressure disguised as this low tritium background, should be guarded against by instrumenting the beds with diagnostics to watch for oxygen, nitrogen, or other reactive gases.

It would be worthwhile to conduct full scale tests on storage beds of these or other reactive metals in the mode of catastrophic rupture to verify predictions of energy release, release rates, and their consequences. These could be effectively done with deuterium on the test bed rather than tritium.

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